

**What is claimed is:**

1           1.    A layered proton exchange membrane, comprising:  
2           an organic/inorganic composite membrane, comprising  
3           inorganic proton conductor and organic base  
4           polymer; and  
5           at least one proton exchange membrane.

1           2.    The layered proton exchange membrane as claimed  
2           in claim 1, wherein the inorganic proton conductor is  $H_3O^+$   
3            $\beta$ -alumina,  $Sb_2O_5 \cdot 5.4H_2O$ , H-modenite, heteropoly acid,  
4           zeolite, zirconium phosphate, silicon oxide, titanium  
5           oxide, tungsten acid, sulfated zirconia, sulfated  
6           alumina, sulfated titanium oxide or sulfated titanium-  
7           aluminum oxide.

1           3.    The layered proton exchange membrane as claimed  
2           in claim 1, wherein the organic base polymer is a proton  
3           conductive polymer.

1           4.    The layered proton exchange membrane as claimed  
2           in claim 1, wherein the organic base polymer and base  
3           material of the proton exchange membrane are polymers  
4           with cationic ion exchange groups.

1           5.    The layered proton exchange membrane as claimed  
2           in claim 4, wherein the polymers with cationic ion  
3           exchange groups are poly(vinylidene fluoride)-grafted-  
4           sulfonated polystyrene (PVDF-g-SPS), PVDF-g-sulfonated-  
5           poly(N-vinylcarbazole), PVDF-g-poly(vinylphosphonic  
6           acid), PVDF-g-poly(4-vinylbenzoic acid), PVDF-g-

7 Sulfonated-poly(2-vinylnaphthalene), or PVDF-g-  
8 Sulfonated-poly(9-vinylanthracene).  
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1 6. The layered proton exchange membrane as claimed  
2 in claim 5, wherein the cationic ion exchange resins are  
3 sulfonate, carboxylate, phosphonate, imide, sulfonimide  
4 or sulfonamide.

1 7. The layered proton exchange membrane as claimed  
2 in claim 1, wherein the organic base polymer further  
3 comprises fluorine-containing resin to form the  
4 organic/inorganic composite membrane.

1 8. The layered proton exchange membrane as claimed  
2 in claim 7, wherein the fluorine-containing resin is  
3 poly(vinylidene fluoride), poly(vinylidene fluoride/  
4 hexafluoropropylene) copolymer, poly(vinylidene fluoride/  
5 chlorotrifluoroethylene) copolymer,  
6 poly(vinylidene fluoride/hexafluoropropylene/tetrafluoro  
7 ethylene) tripolymer or poly(chlorotrifluoro ethylene).

1 9. The layered proton exchange membrane as claimed  
2 in claim 1, wherein the organic base polymer further  
3 comprises non fluorine-containing resin to form the  
4 organic/inorganic composite membrane.

1 10. The layered proton exchange membrane as claimed  
2 in claim 9, wherein the non fluorine-containing resin is  
3 polyacrylate, polyester, polyetherketone, polysulfone,  
4 polyether, polyamide, polyphenylene oxide or polyethylene  
5 oxide.

1           11. The layered proton exchange membrane as claimed  
2           in claim 1, wherein the methanol permeability of the  
3           organic/inorganic composite membrane is less than  $10^{-7}$   
4            $\text{cm}^2/\text{s}$ .

1           12. The layered proton exchange membrane as claimed  
2           in claim 1, wherein the proton conductivity of the  
3           organic/organic composite membrane is at least  $10^{-4}\text{S}/\text{cm}$ .

1           13. A method for preparing a layered proton exchange  
2           membrane, comprising of:

3           (a)forming an organic/inorganic composite membrane  
4           by doping inorganic proton conductor in organic  
5           base polymer; and

6           (b)combining the organic/inorganic complex membrane  
7           and a proton exchange membrane to form a  
8           layered proton exchange membrane.

1           14. The method as claimed in claim 13, wherein the  
2           step (a) is performed by physical blending, chemical  
3           cross-linking, UV radiation cross-linking or sol-gel.

1           15. The method as claimed in claim 13, wherein the  
2           step (b) is performed by thermal pressing, chemical  
3           cross-linking or UV radiation cross-linking.

1           16. The method as claimed in claim 13, wherein the  
2           number of the proton exchange membrane is at least one  
3           and the organic/inorganic composite membrane is located  
4           on one side of the layered proton exchange membrane.

1           17. The method as claimed in claim 13, wherein step  
2           (b) further comprises combining an adhesive film between  
3           the organic/inorganic composite membrane and the proton  
4           exchange membrane.

1           18. The method as claimed in claim 13, further  
2           comprising introducing cationic ion exchange groups into  
3           the layered proton exchange membrane.

1           19. A direct liquid-feed methanol fuel cell,  
2           comprising:  
3           a cathode;  
4           an anode; and  
5           a layered proton exchange membrane, formed by  
6           lamination of an organic/inorganic composite  
7           membrane with at least one proton exchange  
8           membrane, wherein the organic/inorganic  
9           composite membrane comprises organic base  
10          polymer and inorganic proton conductor.

1           20. The direct methanol fuel cell as claimed in  
2           claim 19, wherein the methanol permeability of the  
3           organic/inorganic composite membrane is less than  $10^{-7}$   
4           cm<sup>2</sup>/s.

1           21. The direct methanol fuel cell as claimed in  
2           claim 19, wherein the proton conductivity of the  
3           organic/inorganic composite membrane is at least  $10^{-4}$  S/cm.